



PATENT SPECIFICATION

NO DRAWINGS

1.158.418

Date of Application and filing Complete Specification: 17 Nov., 1966.

No. 51595/66.

Application made in France (No. 38843) on 17 Nov., 1965.

Complete Specification Published: 16 July, 1969.

© Crown Copyright 1969.

Index at acceptance:—B1 E(20Y, 277, 32Y, 321, 322, 34Y, 342, 39Y, 391, 392, 41Y, 412, 413, 42Y, 421, 422, 522, 562, 622)

Int. Cl.:—B 01 j 11/18

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Sect 16 of the Patents Act 1949 are:—JEAN COSYNS and JEAN FRANCOIS LE PAGE both French Citizens of 5 rue de Sannois Nanterre, (Hauts de Seine) France, and of 6 rue Henri Dunant, Rueil Malmaison, (Hauts de Seine), France.

COMPLETE SPECIFICATION

Improved process of Reactivation Applicable to Hydrogenation Catalysts

5 We, INSTITUT FRANCAIS DU PETROLE DES CARBURANTS ET LUBRIFIANTS a French Body Corporate of 1 & 4 Avenue de Bois-Preau, 92 Rueil-Malmaison, (Hauts De Seine), France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to an improved process of reactivation which may be applied to catalysts containing at least a metal of group VIII of the periodic table of elements, such as for instance cobalt, platinum, palladium or 15 nickel deposited on supports and which have lost at least a part of their activity due to their use for selective hydrogenation of highly unsaturated compounds. These catalysts may contain also complementary hydrogenating components, more particularly compounds of elements of group VI such as molybdenum or tungsten oxides or neutralizing compounds such as lime, baryta $Ba(OH)_2$, sodium or potassium oxide.

25 By highly unsaturated compounds is meant acetylenic and conjugated diethylenic hydrocarbons, cyclic or acyclic, which may be converted by selective hydrogenation into monoethylenic hydrocarbons, as well as alkenylaromatic hydrocarbons which may be converted 30 by selective hydrogenation into alkylaromatic hydrocarbons.

35 These hydrocarbons may be subjected to a selective hydrogenation in the form either of chemically well defined and pure substances or of mixtures thereof or in admixture with other hydrocarbons substantially inert in this type of hydrogenation, more particularly saturated hydrocarbons (cyclic or acyclic) monoethylenic

hydrocarbons (cyclic or acyclic) aromatic or 40 alkylaromatic hydrocarbons. This is the case, for example, of cuts obtained from dehydrogenation or pyrolysis processes, especially from cracking or steam-cracking. The highly unsaturated hydrocarbons contain at least 2 carbon 45 atoms in their molecule and sometimes more than 30 carbon atoms, there being no upper limit to this number of carbon atoms. In the most interesting cases this number lies between 3 and 15.

50 The selective hydrogenation, using one of the above mentioned catalysts, is conducted at a temperature comprised generally between 0 and 250°C and preferably between 100° and 190°C.

55 After a certain period of use, these catalysts lose a part of their activity. The reason is not well known but the inventors' work has shown that this deactivation was at least partly due to the deposit of polymeric or rubbery - like materials and, sometimes, to an excessive poisoning of the charge by the impurities especially sulfurous ones.

60 Therefore this deactivation is different from that which is observed with catalysts employed at higher temperatures for example in hydrocracking, hydrofining, reforming or even pure saturating hydrogenation processes.

65 Heretofore the regeneration itself was carried out for example by burning the carbonaceous materials, gums and/or polymers accumulated on the catalyst during its use in selective hydrogenation reactions.

70 Nevertheless, for these catalysts this process is difficult and rarely leads to the restoration of the initial activity and selectivity.

75 Another known method consists of contacting hydrogen with the catalyst, at an elevated

[Price 4s. 6d.]

- temperature, in order to decompose and remove the polymerized products which soiled the catalyst while reducing oxidized or sulfurized compounds of low catalytic activity into the corresponding metal which exhibits a higher catalytic activity in the selective hydrogenation. In fact, it has been observed too that this last method was still insufficient to restore completely the initial activity of the selective hydrogenation catalyst.
- The present invention relates to a new reactivation process whereby the above-mentioned drawbacks are strongly reduced or even completely suppressed.
- According to this process, the deactivated catalyst is, in a first step, washed by a stream of at least one inert liquid hydrocarbon herein defined, at a temperature lower than 200°C, for example between 50 and 150°C, then in a second and subsequent step a stream of hydrogen at a temperature comprised between 200° and 500°C, preferably between 350° and 450° C is circulated through a bed of the washed catalyst.
- By stable or inert hydrocarbon is meant any saturated or monoethylenic hydrocarbon (cyclic or acyclic) or an aromatic or alkylaromatic hydrocarbon (the cycloalkylaromatic hydrocarbons being included) provided that it is in the liquid state under the treatment conditions. These hydrocarbons will usually contain from 3 to 16 carbon atoms and preferably from 6 to 10.
- As specific examples are mentioned: propane, n.butane, isopentane, neopentane, n.heptane, isooctane, n.dodecane, n.hexadecane, cyclohexane, methylcyclohexane, decahydronaphthalene, 2-butene, 1-octene, cyclohexene, benzene, toluene, xylenes, ethylbenzene, 1 - methyl naphthalene. Mixtures of hydrocarbons may be used, for example in the form of an aromatic cut or of a gasoline, which contains neither gums nor unstable compounds such as diolefins, acetylenic or alkenylaromatic compounds. The gasolines obtained by reforming or straight distillation are specially suitable. The presence of aliphatic or cycloaliphatic monoolefins is not harmful.
- The preferred temperature range for the treatment with the table (inert) hydrocarbons is 50—150°C.
- The pressure is chosen sufficient to maintain a liquid phase of said inert hydrocarbon. An overpressure may be established, if necessary, by means of hydrogen or any other inert gas. Usually the absolute total pressure will be in the range of 0.5—200 atmospheres. With a gasoline, for example, the total pressure will be preferably in the range of 5—30 atmospheres.
- The hydrocarbons are circulated through a bed of deactivated catalyst, for example at an hourly rate of 0.5—200 (more preferably 1—10) volumes of liquid hydrocarbons per volume of catalyst. This step takes usually at least 15 minutes and more frequently 1—24 hours.
- A reduction in the weight of the deactivated catalyst is usually observed, due to the dissolution of impurities.
- To follow this washing step, the amount of dissolved gums or sulfur compounds present in the hydrocarbons issued from the washing step may be determined, for example according to A.S.T.M. methods No. D 381—61 T and D 1266 respectively.
- This washing treatment is preferably continued until no more gums or sulfur compounds may be detected in the washing effluent stream.
- The subsequent treatment by means of hydrogen is preferably carried out under an absolute pressure of 1—200 (preferably 2—30) kg/cm² and at an hourly feed rate of gaseous hydrogen of 5—5000 (preferably 50—500) volumes per volume of catalyst (under normal temperature and pressure conditions).
- Hydrogen may be used in a substantially pure state or as a mixture with inert gases, for example as refinery gas. A content of hydrogen of more than 70% by volume is however preferred.
- The following examples are given by way of illustration, not limitation.
- EXAMPLE 1**
- This example describes the reactivation of a catalyst of nickel on alumina which had been used in the selective hydrogenation of a feed charge containing:
- | | | |
|------------|-----------------------------|-----|
| —isoprene: | about 10% (molar) | |
| —benzene: | about 90% (molar) | 100 |
| —sulfur: | 100 parts per million (ppm) | |
- whereof 90 ppm of sulfur from thiophene and 10 ppm of sulfur from mercaptans.
- The catalyst exhibited the following initial composition:
- | | | |
|-----------------------------------|-------------------|--|
| —Al ₂ O ₃ : | 86.6% (by weight) | |
| —Ca O: | 1% " | |
| —Ni O: | 12.4% " | |
- After use, the deactivated catalyst exhibited a 10% increase of its weight as compared with its initial weight.
- Liquid benzene was caused to flow through this deactivated catalyst, under a 28 kg/cm² pressure and at 80°C, the hourly flow rate being 2 volumes per volume of catalyst, and the operation being continued until no more polymerisate is present in the liquid effluent, which takes about 3 hours.
- The injection of benzene is then stopped and and hydrogen is passed therethrough at 400° C under 5kg/cm², at an hourly flow rate of 200—250 liters per litre of catalyst.
- This is continued for 3 hours. All the nickel is thus reduced to the metallic state.

The reactivated catalyst is used to treat the above described feed charge under following conditions (same as the initial conditions):

- 5 —Pressure H_2 : 40 bars
 —Ratio gaseous H_2 /liquid feed: 250 liters/liter
 —T: 100°C
 —Hourly liquid feed rate: 2 volumes/volume of catalyst.

The following Table I shows the results obtained with the reactivated catalyst (A), as compared with those obtained with the fresh catalyst (B), the deactivated catalyst (C) after 1000 hours of use, or the deactivated catalyst reactivated by hydrogen only (D) under the conditions described above (without washing with benzene). 10 15

TABLE I

Catalyst	% conversion of isoprene
Fresh catalyst (B)	99
Deactivated catalyst (C)	89
Reactivated catalyst (A)	99
Reactivated catalyst (D)	95*

* A further treatment by hydrogen does not improve this figure.

EXAMPLE 2

- 20 This example relates to the selective hydrogenation of a steam-cracker gasoline to remove therefrom highly unstable products such as conjugated diolefins and alkenylaromatic hydrocarbons which are gum-producers.

- 25 This gasoline exhibited the following characteristics:

- Distillation A.S.T.M.: 40—270°C
 —Specific weight (g/ml at 20°C): 0.765
 —Sulfur: 5 ppm by weight

- 30 The operating conditions were as follows:

- T: 130°C
 —Pressure H_2 : 28 bars
 —Ratio H_2 /liquid charge: 250 liters/liter
 —Hourly liquid feed rate: 2 volumes/volume of catalyst. 35

The following table II gives the results obtained with the fresh catalyst, the deactivated catalyst (2000 hours of use) and the catalyst reactivated as described for (A) in example 1, except that to benzene was substituted a de-pentanised gasoline containing no unstable compounds and no gums and exhibiting the following characteristics: 40

Composition: Aromatic hydrocarbons: 69% by volume 45
 Saturated hydrocarbons: 31% by volume

Distillation A.S.T.M.: 60—180°C
 Gums present before washing with heptane in mg/100cm³: nul 50

TABLE II

Analysis	Charge	Product		
		with fresh catalyst	with deactivated catalyst	with reactivated catalyst
Bromine number (A.S.T.M. — D. 1159—61)	66	50	58	49.9
Maleic anhydride value (MAV) (U.O.P. method 326.58)	74	0	34	0
Gums present (mg/100cm ³) (A.S.T.M. — D. 381—61T)	25	200	2000	150
Gums present after washing with heptane (mg/100cm ³)	7	7	8	7
Potential gums (mg/100cm ³) (A.S.T.M. — D. 873)	7400	300	3500	150
Octane number clear (research method) (A.S.T.M. — D. 908—58)	98	97	98	97

The analyses were conducted on the crude fraction at the outlet of the reactor, and not after distillation.

feed charge has the same composition as that of example 2.

The first step of the reactivation is carried out with the depentanised gasoline described in example 2. The treatment by means of gasoline and that carried out with hydrogen are the same as described in example 2.

The results are given in Table III.

5

EXAMPLE 3

In this example, several reactivation methods are compared. The treated catalysts are of the same kind as that of example 1 whereas the

10

15

TABLE III

Reactivation process	% conversion of diolefins
No reactivation (deactivated catalyst, after 2000 hours of use)	54
Same deactivated catalyst treated only by gasoline at 80° C. under 28 bars H ₂	55
Same deactivated catalyst treated first by gasoline at 80° C. and 28 bars H ₂ and then by hydrogen at 400° C.	100
No reactivation (deactivated catalyst, after 1500 hours of use)	63
Same deactivated catalyst after reactivation by hydrogen at 400° C.	95
Same deactivated catalyst after reactivation by hydrogen at 400° C. followed by gasoline at 80° C. and 28 bars H ₂	95

In table III, the catalytic activity is measured by the % conversion of diolefins, expressed as:

$$100 \times \frac{\text{MAV}_o - \text{MAV}_{ef}}{\text{MAV}_o}$$

- 5 wherein MAV_o is the maleic anhydride value of the feed charge and MAV_{ef} of the maleic anhydride value of the effluent.

The following may be deduced:

- 10 —1) The reactivation by mere washing with gasoline is inefficient.
 —2) The reactivation by mere hydrogenation is only partial.
 —3) The best results are obtained when the washing by gasoline is carried out before the
 15 hydrogenation, and not the reverse order.

EXAMPLE 4

A selective hydrogenation is carried out on a gasoline of density (d_4^{15}) 0.76, exhibiting a dark color, a bromine number of 72 and a MAV of 73.

The catalyst is palladium.

The hydrogenation is carried out at 50°C and 30 kg/cm² with an hourly liquid feed rate of 4 volumes per volume of catalyst.

The ratio H₂/liquid hydrocarbon is 20 litres
 25 per liter.

After deactivation, the catalyst is regenerated as described in example 1, however the hydrogenation step is carried out at 210°C (and not 400°C).

The following results were obtained.

	Density	Color	Bromine index	MAV
Feed charge	0.760	dark	72	73
Product (fresh catalyst)	0.758	no color	55	2.5
Product (deactivated catalyst)	0.759	no color	65	10
Product (regenerated catalyst)	0.758	no color	59	3.2

WHAT WE CLAIM IS:—

- 35 1—An improved process for reactivating deactivated catalysts containing a group VIII metal, said catalysts having been previously used for the selective hydrogenation of highly unsaturated organic compounds (as hereinbefore defined), said process comprising, in a
 40 first step, washing the deactivated catalyst by means of a stream of at least one inert liquid hydrocarbon (as hereinbefore defined), at a temperature lower than 200°C, and, in a second and subsequent step, circulating a
 45 stream of hydrogen at a temperature in the range of from 200 to 500°C through a bed of this washed catalyst.

- 50 2—A process according to claim 1, wherein the inert hydrocarbon is selected from saturated, monoethylenic, aromatic and alkylaromatic hydrocarbons.

- 3—A process according to claim 1, wherein the deactivated catalyst is washed with a mixture of inert hydrocarbons.

- 55 4—A process according to claim 1, wherein the temperature, in the first step, is comprised between 50 and 150°C.

- 60 5—A process according to claim 1, wherein the washing of the first step is carried out at least until no more gums or sulfur compounds are dissolved in the liquid hydrocarbon.

- 6—A process according to claim 1, wherein

the hourly feed rate of inert liquid hydrocarbon is comprised between 0.5 and 200 volumes
 65 per volume of catalyst.

- 7—A process according to claim 1, wherein the first step washing is carried out for at least 15 minutes.

- 8—A process according to claim 1, wherein the temperature, in the second step, is comprised between 350 and 450°C.

- 9—A process according to Claim 1, wherein the pressure, in the second step, is comprised between 1 and 200 kg/cm².

- 10—A process according to claim 1, wherein the hydrogen hourly feed rate, in the second step, is comprised between 5 and 5000 volumes
 75 per volume of catalyst.

- 11—A process according to claim 1, wherein the catalyst contains nickel and alumina.

- 12—A process according to claim 1, wherein the catalyst contains nickel, molybdenum oxide and alumina.

- 13—A process according to claim 1 wherein the catalyst contains palladium.

- 14—An improved process for reactivating deactivated catalysts containing a group VIII metal, substantially as herein described with reference to any of Examples 1 to 4.

- 15—Reactivated deactivated catalysts whenever prepared by the process of any of claims 1 to 14.

20

25

30

65

70

75

80

85

90

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27, Chancery Lane, London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.